

# Entangled Spin-Orbital Phases in the $d^9$ Model

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We investigate the phase diagrams of the spin-orbital  $d^9$  Kugel-Khomskii model for a bilayer and a monolayer square lattice using Bethe-Peierls-Weiss method. For a bilayer we obtain valence bond phases with interlayer singlets, with alternating planar singlets, and two entangled spin-orbital (ESO) phases, in addition to the antiferromagnetic and ferromagnetic order. Possibility of such entangled phases in a monolayer is under investigation at present.

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It has been shown that quantum fluctuations are enhanced near the orbital degeneracy and could suppress long-range order in the Kugel-Khomskii (KK) model [1], called below the  $d^9$  model. This model was introduced long ago for a perovskite  $\text{KCuF}_3$  [2], a strongly correlated system with a single hole within degenerate  $e_g$  orbitals at each  $\text{Cu}^{2+}$  ion. Kugel and Khomskii showed that orbital order can be stabilized by a purely electronic superexchange mechanism. This happens for strongly frustrated orbital superexchange [3], and columnar Ising-type of order is obtained [4] in the two-dimensional quantum compass model. This model exhibits nontrivial symmetry properties which may be employed to perform efficient calculations for square compass clusters [5].

Orbital order occurs in a number of compounds with active orbital degrees of freedom, where strong Coulomb interaction localizes electrons (or holes) and gives rise to spin-orbital superexchange [6]. When spin and orbital pseudospins couple to each other, their order is usually complementary — alternating orbital (AO) order accompanies ferromagnetic (FM) spin order, and ferro-orbital (FO) order coexists with antiferromagnetic (AF) spin order. However, the above Goodenough-Kanamori rules, see also [3], are not satisfied in cases when spin-orbital entanglement (SOE) dominates [7], as for instance in the spin-orbital  $d^1$  model on a triangular lattice [8].

The spin-orbital superexchange KK model for  $\text{Cu}^{2+}$  ( $d^9$ ) ions in  $\text{KCuF}_3$  with  $S = 1/2$  spins and  $e_g$  orbitals described by  $\tau = 1/2$  pseudospin was derived from the degenerate Hubbard Hamiltonian with hopping  $t$ , intraorbital Coulomb interaction  $U$  and Hund's exchange  $J_H$  [9]. It describes the Heisenberg  $\text{SU}(2)$  spin interactions coupled to the orbital problem by superexchange  $J = 4t^2/U$ ,

$$\mathcal{H} = -\frac{1}{2}J \sum_{\langle ij \rangle || \gamma} \left\{ \left( r_1 \Pi_{\langle ij \rangle}^t + r_2 \Pi_{\langle ij \rangle}^s \right) \left( \frac{1}{4} - \tau_i^\gamma \tau_j^\gamma \right) + r_3 \Pi_{\langle ij \rangle}^s \left( \frac{1}{2} - \tau_i^\gamma \right) \left( \frac{1}{2} - \tau_j^\gamma \right) \right\} - E_z \sum_i \tau_i^z. \quad (1)$$

where  $\{r_1, r_2, r_3\}$  depend on  $\eta \equiv J_H/U$  [9], and  $\gamma = a, b, c$  is the bond direction. In a bilayer two  $ab$  planes are

connected by interlayer bonds along the  $c$  axis [10] (a monolayer has only bonds within a single  $ab$  plane). Here

$$\Pi_{\langle ij \rangle}^s = \frac{1}{4} - \mathbf{S}_i \cdot \mathbf{S}_j, \quad \Pi_{\langle ij \rangle}^t = \frac{3}{4} + \mathbf{S}_i \cdot \mathbf{S}_j, \quad (2)$$

are projection operators on a triplet (singlet) configuration on a bond  $\langle ij \rangle$ , and  $\tau_i^\gamma$  are the orbital operators for bond direction  $\gamma = a, b, c$ . They are defined in terms of Pauli matrices  $\{\sigma_i^x, \sigma_i^z\}$  as follows:

$$\tau_i^{a(b)} \equiv \frac{1}{4} (-\sigma_i^z \pm \sqrt{3}\sigma_i^x), \quad \tau_i^c = \frac{1}{2} \sigma_i^z. \quad (3)$$

Finally,  $E_z$  is the crystal-field splitting which favors either  $x \equiv x^2 - y^2$  (if  $E_z > 0$ ) or  $z \equiv 3z^2 - r^2$  (if  $E_z < 0$ ) orbitals occupied by holes. Thus the model Eq. (1) depends on two parameters:  $E_z/J$  and  $\eta$ .

The spin-orbital model Eq. (1) describes also  $\text{CuO}_2$  planes in  $\text{La}_2\text{CuO}_4$ , where indeed  $U \gg t$  and large  $E_z/J_H \simeq 0.27$  favors holes within  $x$  orbitals [9]. The superexchange between  $\text{Cu}^{2+}$  ions  $\sim 0.127$  eV reproduces there the experimental value. In this paper we consider the model Eq. (1) for  $\text{K}_3\text{Cu}_2\text{F}_7$  bilayer compound where nearly degenerate  $e_g$  orbitals are expected. It has been shown that the magnetic state of  $\text{K}_3\text{Cu}_2\text{F}_7$  is described by interlayer valence bond (VB) phase stabilized by FOz order with  $z$  orbitals occupied by holes [11].

We show below that the bilayer spin-orbital  $d^9$  model Eq. (1) describes a competition between different types of spin-orbital order. Consider first  $|E_z| \rightarrow \infty$ , where depending on the sign of the crystal field  $E_z$  we get either FOz or FOx configuration with  $\langle \tau_i^c \rangle \equiv \pm 1/2$  and  $\langle \tau_i^{a(b)} \rangle \equiv \mp 1/4$ . After inserting these values into Eq. (1) one finds the Heisenberg model describing either an AF bilayer ( $E_z \rightarrow -\infty$ ) or two independent AF planes ( $E_z \rightarrow \infty$ ) as in  $\text{La}_2\text{CuO}_4$ . In the limit of  $\eta \rightarrow (1/3)^-$ , the coefficient  $r_1 = 1/(1 - 3\eta)$  diverges and at large  $\eta > 0.26$  one finds fully FM configuration with AO order.

The simplest approach is a single-site mean field (MF) approximation applied to the model Eq. (1). It excludes any spin fluctuations so the spin projectors  $\Pi_{\langle ij \rangle}^{t(s)}$  ( $\Pi_{\langle ij \rangle}^s$ )

can be replaced by their mean values, where the dependence on the bond  $\langle ij \rangle$  reduces to direction  $\gamma$  in phases with translationally invariant magnetic order listed in Table I: the  $G$ -AF phase, the  $C$ -AF phase with AF planes and FM interplane bonds, the  $A$ -AF phase with FM planes and AF interplane bonds and the FM phase.

In the orbital sector we apply then the MF decoupling for the products  $\{\tau_i^\gamma \tau_{i\pm\gamma}^\gamma\}$  along the axis  $\gamma$ :

$$\tau_i^\gamma \tau_{i\pm\gamma}^\gamma \simeq \langle \tau_i^\gamma \rangle \tau_{i\pm\gamma}^\gamma + \tau_i^\gamma \langle \tau_{i\pm\gamma}^\gamma \rangle - \langle \tau_i^\gamma \rangle \langle \tau_{i\pm\gamma}^\gamma \rangle. \quad (4)$$

As order parameters we take  $t^a \equiv \langle \tau_1^a \rangle$  and  $t^c \equiv \langle \tau_1^c \rangle$  for a chosen site  $i = 1$  (which is sufficient in orbital sector as  $t^b = -t^a - t^c$ ) and we assume two orbital sublattices: each neighbor of the site  $i$  is rotated by  $\pi/2$  in the  $ab$  plane meaning that  $\langle \tau_{i+\gamma}^{a(b)} \rangle = t^{b(a)}$ . The self-consistency equations can be solved analytically (see Ref. [10]) and the phase diagram of Fig. 1(a) is obtained by comparing the ground state energies for different points in the  $(E_z/J, \eta)$  plane. One finds two classes of solutions: (i) uniform orbital configurations ( $t^c = \pm 1/2$ ,  $t^{a(b)} = \mp 1/4$ ) for global FO order, and (ii) nontrivial AO order with orbitals staggering from site to site in  $ab$  planes.

For  $\eta = 0$  we have only two AF phases, see Fig. 1(a):  $G$ -AF $z$  for  $E_z < -J/4$  and  $G$ -AF $x$  for  $E_z > -J/4$ , with different FO orders involving  $z$  or  $x$  orbitals, respectively. Because of the planar orbital configuration in the latter  $G$ -AF phase one finds no interplane spin coupling and thus this phase is degenerate with the  $C$ -AF one. For higher  $\eta$  the number of phases increases abruptly by three phases, all with AO configurations: the  $A$ -AF,  $G$ -AF/AO and  $C$ -AF/AO phase. Surprisingly, the AO version of the  $G$ -AF phase is connected neither to FO $z$  nor to FO $x$  order in an antiferromagnet, excluding the multicritical point at  $(E_z/J, \eta) = (-0.25, 0)$ , and disappears completely for  $\eta \approx 0.118$ . The  $C$ -AF/AO phase stays on top of uniform  $G(C)$ -AF phase, lifting their degeneracy at relatively large  $\eta$  and then gets replaced by the FM phase which always coexists with AO order, so one can conclude that the  $G$ -AF/ $C$ -AF degeneracy is most easily lifted by turning on the orbital alternation. On the opposite side (for  $E_z < 0$ ), the  $G$ -AF $z$  phase is completely surrounded by  $A$ -AF phase with AO order. In the  $A$ -AF phase the AF correlations in the  $c$  direction survive despite the overall FM tendency when  $\eta$  grows. This follows from the orbitals' elongation in the  $c$  direction which

TABLE I. Mean values of triplet and singlet spin projection operators (2) for a bond  $\langle ij \rangle$  in the  $ab$  plane and along the axis  $c$  in magnetic phases with long range order, see Fig. 1.

	average	$G$ -AF	$C$ -AF	$A$ -AF	FM
$ab$ plane	$\langle \Pi_{ij}^t \rangle$	1/2	1/2	1	1
	$\langle \Pi_{ij}^s \rangle$	1/2	1/2	0	0
$c$ axis	$\langle \Pi_{ij}^t \rangle$	1/2	1	1/2	1
	$\langle \Pi_{ij}^s \rangle$	1/2	0	1/2	0

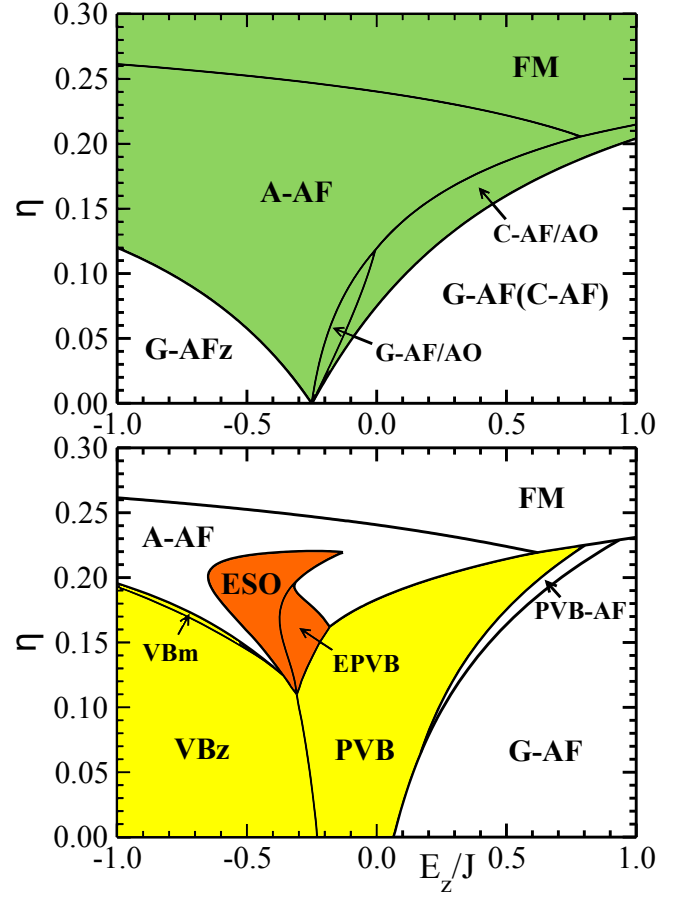


FIG. 1. Phase diagrams of the  $d^9$  bilayer model (1) obtained in: (a) a single-site MF, and (b) a cluster MF. In (a) shaded (green) area indicates phases with nontrivial AO order while the other ones have FO order. In (b) light shaded (yellow) area marks singlet phases with spin disorder and dark (orange) shading indicates phases with SO entanglement.

stabilizes interplane singlets in a better cluster MF approach, see below. Finally, the FM phase is favored for any  $E_z$  if only  $\eta$  is sufficiently close to  $1/3$ , as expected.

In a better cluster MF (or Bethe-Peierls-Weiss) approach, introduced to capture the effects of quantum fluctuations, one divides the bilayer square lattice into separate cubes containing 8 sites each and treats the bonds inside a cube exactly, and the bonds connecting different cubes in MF. This approach has at least three advantages over the single-site MF: (i) spins can fluctuate, (ii) elementary cell can double, and (iii) we can have independent spin-orbital order parameter. The MF leads in a cluster to three order parameters: magnetic  $\langle s \rangle \equiv S_1^z$ , orbital  $t^{a(b)}$ , and on-site SOE  $r^{a(b)} \equiv \langle S_1^z \tau_1^{a(b)} \rangle - s t^{a(b)}$ .

The self-consistency equations take rather complicated form (for details see Ref. [10]) and can be solved only numerically by time-consuming iterative Lanczos diagonalization of a cluster combined with updating the MFs. In orbital sector apart from the AO order described ear-

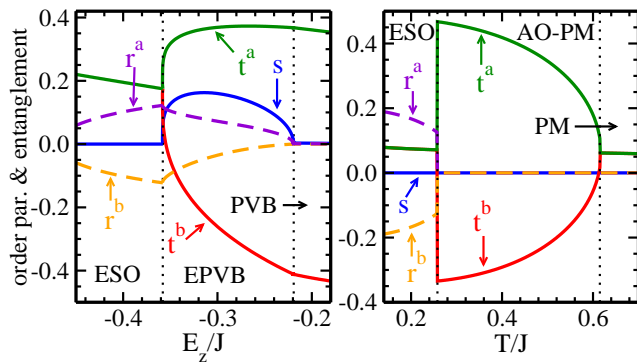


FIG. 2. Order parameters spin  $s$ , orbital  $t^{a(b)}$  and on-site SOE  $r^{a(b)}$  for  $\eta = 0.15$  and for increasing: (a)  $E_z$  in a bilayer in the ESO, EPVB and PVB phase, for  $T = 0$ ; (b)  $T$  in a monolayer in the ESO, AO-PM and PM phase, for  $E_z = -0.6J$ .

lier, we consider configurations where orbitals within a cluster break the symmetry between  $a$  and  $b$  directions but the neighboring clusters are rotated by  $\pi/2$  in the  $ab$  plane, so globally the symmetry is preserved and the elementary cell is doubled. In the spin sector we consider the same configurations as in a single-site approach.

Including spin fluctuations in the cluster MF approach stabilizes the  $G$ -AF phase with  $x$  orbitals over the FM one ( $E_z > 0$ ) but suppresses it when  $z$  orbitals are filled by holes ( $E_z < -J/4$ ), and gives instead three singlet VB phases called: PVB (plaquette VB), VB $z$  and VB $m$ , see Fig. 1(b). VB $z$  phase replaces  $G$ -AF $z$  phase shown in Fig. 1(a) and involves interplane singlets accompanied by FO $z$  configuration. This phase was observed in  $K_3Cu_2F_7$  by Manaka *et al.* [11] — here we explain it for realistic  $\eta \simeq 0.14$ . The VB $m$  phase is very similar to VB $z$  but with slightly modified FO order by an AO component increasing toward the  $A$ -AF phase. Transition from VB $m$  to VB $z$  is of the second order. In the PVB phase spin singlets are pointing uniformly in  $a$  or  $b$  direction within the cluster and the elementary cell is doubled.

A different class of phases involves SOE — these are the ESO, EPVB and PVB-AF phase. All of them exhibit SOE but only the ESO and EPVB ones lie in the highly frustrated part of the phase diagram and have large on-site entanglement  $r^{a(b)}$ , as shown in Fig. 2(a). The PVB-AF phase connects PVB and  $G$ -AF phases by second order phase transitions and is characterized by fast changes in orbital order and appearance of global magnetization. The ESO phase has no magnetization and FO order is here much weaker than in the VB $z$  phase. When  $E_z$  grows, the ESO phase does change continuously into the EPVB configuration, being an entangled precursor of the PVB phase, with doubling of the unit cell and finite AF order which vanishes smoothly approach-

ing the PVB phase. Additional calculations described in [10] show that these entangled phases are absent if one assumes that  $\langle S_1^z \tau_1^{a(b)} \rangle$  factorizes, i.e.,  $r^{a(b)} = 0$ .

Using the same cluster MF approach as above one can easily study the phase diagram of the KK model for a single layer at finite temperature  $T$ . At  $T = 0$  one finds the AF, FM, and PVB phases together with an ESO phase between the AF and FM phases. Turning on the thermal fluctuations we have found that typically the orbital order is much more robust than the magnetic one and the orbital configuration compatible with lattice geometry can greatly stabilize spin order. In Fig. 2(b) we present the thermal evolution of the order parameters  $\{s, t^{a(b)}\}$  and on-site SOE parameter  $r^{a(b)}$  in the ESO phase which melts and ends up as an ordinary paramagnetic (PM) phase. More details and the phase diagrams will be reported elsewhere.

Summarizing, we have shown that spin-orbital entanglement leads to exotic types of order which are stabilized by quantum fluctuations both in bilayer and monolayer systems.. They emerge from highly frustrated spin-orbital superexchange and could be discovered only within a cluster mean field approach.

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